3120 *Macromolecules* **2010**, *43*, 3120–3121
DOI: 10.1021/ma902673z

Macromolecules
NOTE

Phase Diagrams of Stereocontrolled Poly(*N*,*N*-diethylacrylamide) in Water

Yukiteru Katsumoto,* Yuki Etoh, and Naotsugu Shimoda

Graduate School of Science, Hiroshima University, 1-3-1 Kagami-yama, Higashi-Hiroshima 739-8526, Japan

Received December 3, 2009; Revised Manuscript Received January 18, 2010

Thermosensitive polymers, which change physical properties depending upon temperature, are of interest for both polymer science and engineering.[1,2] Poly(*N*-substituted acrylamide) is a representative of thermosensitive polymers in aqueous media.[1,3] In general, the thermoresponsiveness of polymer is concerned with the phase behavior of the polymer solution. Poly(*N*,*N*-diethylacrylamide) (PNdEA) exhibits a lower critical solution temperature (LCST)-type phase behavior in water. It has been generally considered that the phase behavior of PNdEA in water is similar to that for an aqueous solution of poly(*N*-isopropylacrylamide) (PNiPA), which is very popular and widely investigated as a stimuli-responsive polymer.[4−7] Indeed, the salt effects on the phase separation temperature (T_{ps}) of the aqueous solutions of PNdEA and PNiPA are similar to each other.[8] The effects of cosolvent are different for the two polymers; the cononsolvency is found for PNiPA in water−methanol mixtures whereas it is not for PNdEA.[9] A single chain of PNiPA in water undergoes a thermally induced coil−globule transition before the system reaches T_{ps},[10,11] whereas PNdEA chains are not monodispersed and form aggregates even if the system is in the one phase region.[12] These dissimilarities may arise from the difference in the chemical structures of these polymers.

How does the tacticity affect the solution properties of these two polymers? Recently, it has been revealed that the tacticity of PNiPA impacts the phase behavior of the aqueous polymer solution.[13−15] This implies that the solubility of poly(*N*-substituted acrylamide)s is influenced not only by the hydrophilicity of the side chain but also by the stereosequence in the polymer chain. For PNdEA, the systematic investigation on tacticity effects has not been completed. Freitag et al.[16] and Kobayashi et al.[17] have described the tacticity effects on the phase behavior of PNdEA in water. In their reports, however, the other molecular parameters such as the molecular weight (M_n), polydispersity(M_w/M_n), and end groups may make it difficult to uncover the tacticity effects. In this work, therefore, a stereospecific living radical polymerization has been carried out for preparing a set of PNdEA samples with different meso content (*m*) but similar M_n and M_w/M_n. In the present note, we report for the first time the tacticity effect on the phase boundary curve of the aqueous PNdEA solution.

PNdEA samples were prepared by a stereospecific living radical polymerization using reversible addition−fragmentation chain transfer (RAFT) agent and Lewis acid.[18] *N*,*N*-Diethyl-*s*-thiobenzoylthiopropionamide (DETP) used as a RAFT agent was synthesized according to the literatures.[19−21] NdEA monomer was kindly provided by Kojin and purified by distillation under reduced pressure. α,α-Azobisisobutyronitrile (AIBN) was purchased from Wako and recrystallized from methanol. M_n and M_w/M_n of polymer samples were determined by size exclusion chromatography (SEC) (Jasco Intelligent HPLC system) equipped with a guard column (SB-807 HQ, Shodex), two linear poly(hydroxy methacrylate) beads column (Shodex SB-802.5 HQ and SB-806M), and a differential refractive-index detector (RI-2031, Jasco). The eluent was *N*,*N*-dimethylformamide (LiBr 10 mM) at 60 °C with a flow rate of 0.35 mL min^{-1}. A SEC chromatogram was calibrated with standard polystyrene samples. ^{1}H NMR spectra were recorded on a JEOL JNM-LAMBDA spectrometer (500 MHz). The tacticity of the samples was represented by the *m* diad content, which is determined from the methylene proton peaks of the polymer measured in DMSO-d_6 at 140 °C.[16,18] The temperature dependence of transmittance of 650 nm light was monitored by a homemade apparatus equipped with a Si photo diode detector (S2386-18K, Hamaphoto). The temperature was controlled by a homemade thermostat with an accuracy of ±0.1 °C. Heating and cooling rates were < 0.2 °C min^{-1}. The cloud point (T_c) was estimated by second derivative of the transmittance curves.

Table 1. Characterization of Stereocontrolled PNdEAs

ID	M_n/g mol^{-1}	M_w/M_n	*m*	Lewis acid[a]
e-*m*58r[b,c]	5.1×10^4	1.25	58	
e-*m*68r[b,d]	5.2×10^4	1.28	68	Sc(OTf)$_3$
e-*m*82r[b,e]	4.7×10^4	1.23	82	Y(OTf)$_3$
E-*m*55r[b,d]	1.7×10^5	1.66	55	
E-*m*75r[b,d]	1.5×10^5	1.68	75	Y(OTf)$_3$

[a] [Metal trifluoromethanesulfonate] = 0.1 M. [b] [NdEA] = 2.0 M, [AIBN] = 0.8 mM, [DETP] = 8.5 mM. r.t. 60 °C. [c] In benzene. [d] Bulk polymerization. [e] In methanol/toluene(1/1, v/v) mixture.

Table 1 compiles the characterization results of the stereocontrolled PNdEAs. The stereospecific RAFT polymerization makes it possible to prepare a set of samples that have similar M_n and M_w/M_n but different *m*. Because the molecular weight and polydispersity of the samples in each set are very close to each other, we can focus on the tacticity effect of PNdEA on the phase separation behavior. Figure 1A,B depicts the transmittance curves for 1 wt % aqueous solutions of stereocontrolled PNdEAs, indicating that T_c goes up with increasing *m*. The difference in T_c observed for e-*m*55r and E-*m*58r may be involved in not only the tacticity but also the molecular weight and polydispersity. It has been known for an atactic PNdEA that T_c strongly depends on M_n when $M_n < 4.0 \times 10^5$ g mol^{-1}.[22] The result obtained here clearly suggests that thermoresponsiveness of PNdEA is also influenced by the diad tacticity. For example, the T_c of e-*m*82r is higher than that of e-*m*58r by 7 °C. An attractive interaction between the polymer chain and water is weakened at higher temperature, resulting in the LCST phase separation.[23,24] In this context, we have presumed that a *m*-rich PNdEA is more hydrophilic than an atactic one. This tendency is opposite to the tacticity effects on the hydrophilicity of stereocontrolled PNiPA; a *m*-rich PNiPA is more hydrophobic than an atactic one.[13,15] For an aqueous solution of PNiPA, the transmittance curve becomes broader as *m* increases,[15] whereas that for stereocontrolled PNdEAs always shows a steep change at T_c throughout the experiments.

---

*Corresponding author. E-mail: katsumot@hiroshima-u.ac.jp.

Published on Web 02/01/2010

© 2010 American Chemical Society

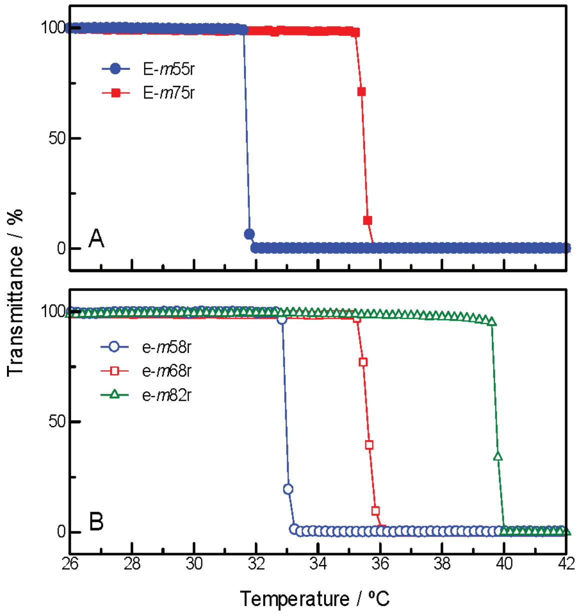

Figure 1. (A) Temperature dependence of transmittance of 650 nm light for the aqueous solutions of stereocontrolled PNdEAs for E-*m*55r (●) and E-*m*75r (■). (B) Transmittance curves for e-*m*58r (○), e-*m*68r (□), and e-*m*82r (△).

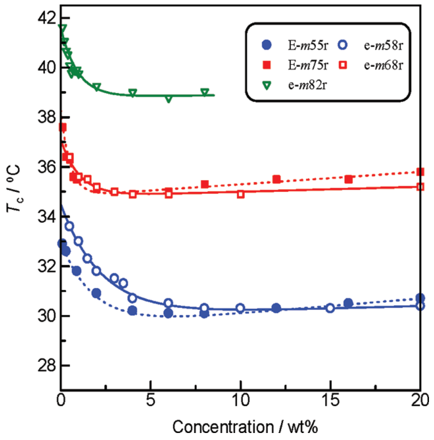

Figure 2. Cloud-point temperature (T_c) plotted against the concentration of PNdEAs, e-*m*58r (○), e-*m*68r (□), e-*m*82r (▽), E-*m*55r (●), and E-*m*75r (■) in water. The solid and dotted lines are drawn as guides for the eyes.

Figure 2 shows the phase boundary curves for the stereocontrolled PNdEAs in water. For both E and e series of samples, the phase boundary curve shifts to higher temperature with increasing *m*. In addition, the shape of the phase boundary curve seems to slightly change depending upon the *m* value. Interestingly, the tacticity dependence of the shape of the phase boundary curve for PNiPA in water is more pronounced than that for PNdEA. For the sample with a smaller M_n ($\sim 5 \times 10^4$), T_c becomes insensitive to the concentration at a higher concentration region, whereas for the sample with M_n ($\sim 1.5 \times 10^5$), T_c gradually increases. Lessard et al. have reported a similar observation for an atactic PNdEA in water.[22] Okada and Tanaka[23] have theoretically reproduced the flat LCST coexistence line for an aqueous polymer solution by using a lattice model in which the cooperative hydration of the polymer chain is considered. According to this theory, the phase boundary curve for aqueous polymer solutions becomes flatter as the cooperativity of hydration is strengthened.

The present study has clearly revealed that the tacticity plays an important role in the phase separation behavior of PNdEA in water. The phase boundary curve is discernibly changed by a small difference in *m*. We revealed that the tacticity effect on T_c for PNdEA in water is distinctly different from that for PNiPA in water.

Acknowledgment. This work was partially supported by the Grant-in-Aid for Young Scientists (B) (no. 21750126).

Supporting Information Available: Syntheses of *N*,*N*-Diethyl-*s*-thiobenzoylthiopropionamide (DEPT), evolution of M_n and M_n/M_w with conversion for DEPT-mediated polymerization of PNdEA, NMR spectra and SEC charts of polymer samples, and concentration dependence of the transmittance curves of stereocontrolled PNdEA in water. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gil, E. S.; Hudson, S. M. *Prog. Polym. Sci.* **2004**, *29*, 1173.
(2) Lutz, J.-F.; Akdemir, Ö.; Hoth, A. *J. Am. Chem. Soc.* **2006**, *128*, 13046.
(3) Shild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(4) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441.
(5) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(6) Tong, Z.; Zeng, F.; Zheng, X.; Sato, T. *Macromolecules* **1999**, *32*, 4488.
(7) de Azevedo, R. G.; Rebelo, L. P. N.; Ramos, A. M.; Szydlowski, J.; de Sousa, H. C.; Klein, J. *Fluid Phase Equilib.* **2001**, *185*, 189.
(8) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352. Idziak, I.; Avoce, D.; Lessard, D.; Gravel, D.; Zhu, X. X. *Macromolecules* **1999**, *32*, 1260.
(9) Maeda, Y.; Nakamura, T.; Ikeda, I. *Macromolecules* **2002**, *35*, 10172. Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Macromolecules* **1990**, *23*, 2415.
(10) Kubota, K.; Fujishige, S.; Ando, I. *J. Phys. Chem.* **1990**, *94*, 5154.
(11) Chi, W.; Zhou, S. *Macromolecules* **1995**, *28*, 8381.
(12) Itakura, M.; Inomata, K.; Nose, T. *Polymer* **2000**, *41*, 8681.
(13) Ray, B.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M.; Seno, K.; Kanaoka, S.; Aoshima, S. *Polym. J.* **2005**, *37*, 234.
(14) Hirano, T.; Okumura, Y.; Kitajima, H.; Seno, M.; Sato, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4450.
(15) Katsumoto, Y.; Kubosaki, N. *Macromolecules* **2008**, *41*, 5955.
(16) Freitag, R.; Baltes, T.; Eggert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 3019.
(17) Kobayashi, M.; Ishizone, T.; Nakahama, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4677.
(18) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702.
(19) Rademacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J. *Macromolecules* **2000**, *33*, 284.
(20) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2000**, *35*, 8300.
(21) The procedure can be found in Supporting Information.
(22) Lessard, D. G.; Ousalem, M.; Zhu, X. X. *Can. J. Chem.* **2001**, *79*, 1870.
(23) Okada, Y.; Tanaka, F. *Macromolecules* **2005**, *38*, 4465.
(24) Ono, Y.; Shikata, T. *J. Am. Chem. Soc.* **2006**, *128*, 10030.